

Minerals of Jenolan Caves, New South Wales, Australia: Geological and Biological Interactions

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Geological and biological processes in the Jenolan Caves have formed a range of mineral species spanning several chemical groups. So far 25 mineral species have been either confirmed, or identified for the first time at Jenolan. Their chemical groups include carbonates: (calcite, aragonite, hydromagnesite, huntite, dolomite, ankerite); silicates: (kaolinite, K-deficient muscovite ('illite'), montmorillonite clays); phosphates, (ardealite, hydroxylapatite, taranakite, leucophosphite, variscite, crandallite, montgomeryite, kingsmountite); sulfate: (gypsum); oxides: (quartz, cristobalite, amorphous silica, hematite, romanèchite); hydroxide: (goethite); nitrate: (niter); and chloride: (sylvite). Dolomitised limestone bedrock and ankerite veins can be recognised as a magnesium source of some magnesium carbonate minerals, as well as supplying a calcite inhibitor favouring aragonite formation. The cave clays have diverse origins. Some are recent sedimentary detritus. Older clays of Carboniferous age contain components of reworked altered volcanoclastics washed or blown into the caves, so these clays may represent argillic alteration of volcanic products. Some of the clays may have formed as alteration products of ascending hydrothermal fluids. The phosphates and some gypsum formed when bat guano reacted chemically with limestone and cave clays. Gypsum has also been formed from the breakdown of pyrite in altered bedrock or dolomitic palaeokarst. The niter and sylvite have crystallized from breakdown products of mainly wallaby guano.

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KEYWORDS: biology, geology, guano, Jenolan Caves, minerals

INTRODUCTION

The Jenolan Caves, 182 km west of Sydney in the Greater Blue Mountains World Heritage Area, are developed in the folded, steeply dipping, Late Silurian Jenolan Caves Limestone (Carne and Jones 1919; Chalker 1971; Allan 1986), and in places intersect stratified Palaeozoic marine carbonate palaeokarst deposits, termed caymanite (Osborne 1991, 1993, 1994). The Jenolan Caves Limestone extends 7 km in a NW direction, in the valley of McKeown's Creek, having a maximum thickness of 265 m. The caves are developed on the northern and southern sides of the Grand Arch, a natural tunnel cutting the limestone.

From the discovery of Jenolan Caves by Europeans after 1838, the calcite speleothems have been admired for their beauty and variety, but other minerals were not recognised until the late 19th Century,

when niter was first reported by Wilkinson (1886), and gypsum and phosphate minerals by Mingaye (1898). An Australian Museum-Sydney University project to characterise the minerals of Jenolan Caves has been active for over 25 years, and so far has either confirmed, or identified for the first time at Jenolan, 25 mineral species. Some of the minerals have been formed by completely inorganic chemical processes, but others have involved chemical interactions with biological materials such as marsupial and bat guano. Mineral species in the nitrate, chloride, carbonate, phosphate, sulfate, silicate, oxide and hydroxide chemical groups are described.

MATERIALS AND METHODS

The studied mineral specimens, collected by the authors over the last 25 years, are lodged in the Australian Museum Geoscience collections. Earlier

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cave mineral specimens were donated to the Australian Museum by J.C. Wiburd in 1898 and by others in the late 19th and early 20th centuries. Specimen registration numbers prefixed by 'D' or 'DR' are in the Australian Museum Mineralogy and Petrology collections respectively, and other designations are specimen field collection numbers.

The minerals were identified using a variety of methods, including field observations and analytical methods. Most of the identifications were carried out at the Australian Museum using X-ray diffraction (XRD) equipment (PANalytical X'Pert Pro) with a graphite monochromator, proportional counter, and 45 kV, 40 mA Cu-K α radiation. Scans were run from 5-70° 2 θ with 1° divergence slit, 2° antiscatter slit, 0.1 mm receiver slit and 0.02° steps, with additional scans 2-15° 2 θ with 0.125° divergence slit and 0.25° antiscatter slit. Peak patterns were processed using PANalytical X'Pert HighScore software.

X-ray fluorescence analysis was carried out at the University of Technology, Sydney, using an Rh target at 60 kV, 40 mA, LiF 420, LiF 220, Ge 111 and TIAP analysing crystals, and Siemens UniQuant software. Energy dispersive X-ray spectrometry (EDS) was carried out at the Australian Museum, with an Oxford Instruments Link Isis 200 EDS coupled with a Cambridge Stereoscan 120 SEM, with internal Co standard, in backscatter electron mode. Spectra were accumulated for 100 seconds at 20 kV, 18 – 25 x magnification, and 20 microsecond processing time. SEM imaging was performed at the Australian Museum with a Leo 435VP and later a Zeiss EVO LS 15, using gold coated samples mounted on standard SEM stubs, at 15-20 kV and 18 – 23 mm working distance.

Laser Raman spectroscopy was performed at the Queensland University of Technology using a Renishaw 1000 Raman system, with a monochromator, filter system, CCD detector (1024 pixels) and Olympus BHSM microscope equipped with 10x, 20x, and 50x objectives. The spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm⁻¹ and precision of ± 1 cm⁻¹ in the range between 200 and 4000 cm⁻¹. Repeated acquisitions using a 50 x microscope objective were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. The spectra of at least 10 crystals were collected to ensure the consistency of the data. Infrared spectra were collected at the Queensland University of Technology using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra

over the 4000 - 525 cm⁻¹ range were collected with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm s⁻¹. Spectra (128 scans) were co-added to improve the signal to noise ratio.

Other methods used were polarized light microscopy, ultraviolet fluorescence, K-Ar dating (CSIRO Petroleum) and fission track dating (Geotrack International), inductively-coupled plasma mass spectrometry (University of Cape Town), and sulfur and oxygen isotope determinations (Environmental Isotopes, Sydney, and University of Barcelona).

RESULTS

The following species catalogue documents the rich mineralogical diversity of Jenolan Caves, including physical descriptions and mode of occurrence for those minerals known up to July 2013. The species and their formulae are listed in Table 1.

Calcite

Calcite is the trigonal form of calcium carbonate. It is the main mineral in the Jenolan Caves Limestone, which has an average composition of 97.6% CaCO₃ (Susmilch and Stone 1915; Carne and Jones 1919; Chalker 1971; Allan 1986). It also contains small and variable amounts of Mg and Fe. It forms the majority of cave speleothems in an incredible variety of forms, including stalactites, stalagmites, columns, straws, shawls, shields, canopies, helictites, cave pearls, rim pools, pool crystal, rafts, cave coral and flowstone. The spectacular calcite speleothems are the main features of Jenolan Caves, and a selection is shown in Fig. 1:a,b,c,d,e. Calcite is also deposited through interaction between colonies of blue-green algae (cyanobacteria) and drip water, forming rounded, crenulated stalagmites (stromatolites or 'craybacks') found in Nettle Cave (Fig. 2) and the Devil's Coach House. A speleothem classification is presented in Hill and Forti (1997).

Calcite also forms curious fluffy growths of tangled microcrystalline filaments. They form light insubstantial masses of 'fairy floss' or cotton wool appearance (Fig. 3a) and have been observed up to 5 – 6 cm diameter. When damp the masses are coherent, but fall apart to a white powder when dry. SEM images of these fluffy growths from Wilkinson Branch of Chifley Cave show microcrystalline aggregates of tangled filaments 0.5–1 micron diameter (Fig. 3b). It often grows on a porous mud or clay substrate, but can also cover rock, flowstone and stalactites. It is mainly calcite, with minor silica and water. They have been aptly described by (Mingaye 1899:330):

Table 1: Identified Jenolan Caves mineral species
Chemical formulae are from the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification approved list. The ‘illite series’ chemical formula is from Rieder et al. (1998).

ankerite	$\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$
aragonite	CaCO_3
ardealite	$\text{Ca}_2(\text{PO}_3\text{OH})(\text{SO}_4) \cdot 4\text{H}_2\text{O}$
calcite	CaCO_3
crandallite	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$
cristobalite	SiO_2
dolomite	$\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2$
goethite	$\text{Fe}^{3+}\text{O}(\text{OH})$
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
hematite	Fe_2O_3
huntite	$\text{CaMg}_3(\text{CO}_3)_4$
hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$
kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
kingsmountite	$(\text{Ca}, \text{Mn}^{2+})_4(\text{Fe}^{2+}, \text{Mn}^{2+})\text{Al}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 12\text{H}_2\text{O}$
leucophosphate	$\text{KFe}^{3+}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$
montgomeryite	$\text{Ca}_4\text{MgAl}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 12\text{H}_2\text{O}$
montmorillonite	$(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
muscovite, K-deficient	(“illite series”) $\text{K}_{0.65}\text{Al}_{2.0}\square\text{Al}_{0.65}\text{Si}_{3.35}\text{O}_{10}(\text{OH})_2$
niter	KNO_3
quartz	SiO_2
romanèchite	$(\text{Ba}, \text{H}_2\text{O})_2(\text{Mn}^{4+}, \text{Mn}^{3+})_5\text{O}_{10}$
sylvite	KCl
taranakite	$\text{K}_3\text{Al}_5(\text{PO}_3\text{OH})_6(\text{PO}_4)_2 \cdot 18\text{H}_2\text{O}$
variscite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$

“Two samples of this substance were received. The first, which weighed 1½ grammes, Guide Wiburd states, was compressed into a small match-box, and would fill your hat in its natural state. It is so light that, when you blow on it, it falls off the roof and sides like snow”.

Aragonite

Aragonite, the orthorhombic form of calcium carbonate is the second most common cave mineral world-wide (Hill and Forti 1986, 1997), although its occurrence is still relatively rare. Aragonite crystal groups are highly regarded for their aesthetic value and can form some of the most spectacular of all speleothems (Fig. 4).

At Jenolan, aragonite forms white stalactites, straws, columns, helictites, needles, ‘flos ferri’ and anthodites (quill-like crystal sprays). It is found in a number of caves, including Ribbon (the Lyrebird’s Nest), Pool of Cerberus (the Arabesque), River (the Furze Bushes), Jubilee, Red, Chevalier, Wiburd’s Lake, Mammoth, Spider, Glass, Contact and Barralong Caves (Rowling 2004, 2005a,b). It

occurs on limestone cave walls, palaeokarst deposits and cave clays.

Dolomite

Veins of iron-bearing dolomite intersect the Jenolan Caves Limestone and one bed towards the top of the Limestone is extensively dolomitised. An Fe-rich dolomite mass can be seen just in front of the entrance to the Lyrebird’s Chamber, Ribbon Cave. Near the western edge of the Jenolan Caves Limestone in Contact Cave, dolomitic stalactites are currently forming. Dolomitic palaeokarst (caymanite) occurs extensively in the Mud Tunnels section of River Cave.

Ankerite

Ankerite forms thin yellow to brown branching veins up to several tens of centimetres length in the limestone (Fig. 5), and can also form larger zones of replacement. Ankerite also mantles some of the fossils in the limestone. Much of the veining has a surface alteration to goethite and clays, sometimes

with minor silica. The unaltered material has a sugary texture due to small rhombohedral crystals of ankerite up to 0.3 mm.

Huntite and hydromagnesite

These two minerals are the major components of a Mg-carbonate-rich ‘moonmilk’, a white, structureless, plastic, spongy mass with high water content, sometimes with a ‘cauliflower’ appearance, and having the consistency of cottage cheese when damp, but falling apart as a white powder when dry. Huntite and hydromagnesite with minor calcite, aragonite, and silica have been observed as a 4 cm mass growing on an aragonite stalactite in the Lyrebird’s Nest, Ribbon Cave. Under SEM, this moonmilk shows rosettes of platy crystals up to about 5 microns (Fig. 6). Traces of huntite and hydromagnesite have been found in Wiburd’s Lake Cave (Rowling 2005b).

Clays (Kaolinite, K-deficient muscovite (“illite”), montmorillonite)

Cave clays of plastic consistency and white, yellow, brown and red colours are widespread. Most

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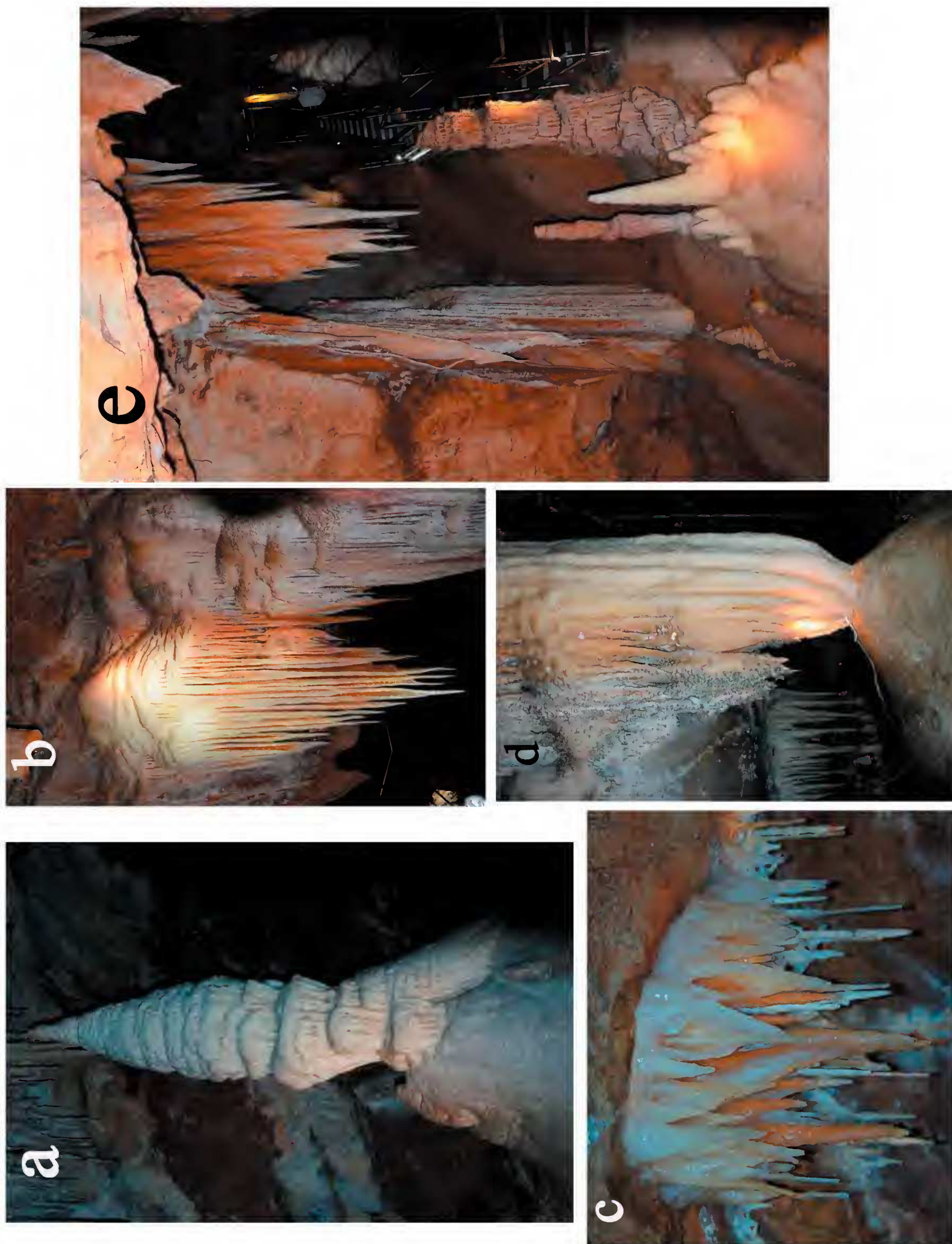


Figure 1a,b,c,d,e:
Calcite speleothems
a: Minaret, River
Cave;
b: Indian Canopy,
Orient Cave;
c: Stalactites, Rib-
bon Cave;
d: Fluted Column,
Imperial Cave;
e: Indian Chamber,
Orient Cave.
Images: Ross
Pogson, Australian
Museum



Figure 2: Stromatolites ('craybacks'), Nettle Cave, width approx. 1.5 m. Image: Ross Pogson, Australian Museum

are kaolinite/illite mixtures, often with quartz, and sometimes with minor calcite or montmorillonite, and coloured by hematite or goethite.

As well as massive forms, kaolinite can also form pseudo-hexagonal crystals up to 3 microns (Fig. 7a), and also pseudomorphs tiny feldspar crystals of possible volcanic origin, in pink clay (DCH4) from the Devils Coach House. Illite forms delicate fluffy or hairy growths on kaolinite (Fig. 7b).

Ardealite

Rounded yellow bosses up to about 9 cm high, called 'potatoes' by Foster (1890); Trickett (1905); and Havard (1928), form the "Potato Patch" of Dunlop (1979), in the Bone Cave section of Lucas Cave (Fig. 8a,b). Similar deposits occur in the Grotto Cave section of Chifley Cave (Fig. 8c), and were reported by Mingaye (1898, 1899). He analysed but did not name the ardealite, identified the accompanying gypsum, and noted that similar deposits were seen in the Bone Cave, Lucas Cave. The 'potatoes' have a thin outer shell of gypsum, but their interiors are filled with softer cream-coloured powdery ardealite,

and minor calcite. They sit on a layer of mixed ardealite, gypsum and hydroxylapatite. Although they sit on a sloping surface, they display a vertical growth axis and may have been deposited under subaerial conditions by vertically-drawn solutions (Pogson et al. 2011). Ardealite is uncommon in Australia, but Bridge (1967) and Bridge et al. (1975) reported ardealite with brushite from Marooba Cave, Jurien Bay, Western Australia, and Grimes (1978) identified ardealite from Texas Caves, Queensland, all with guano associations.

Hydroxylapatite

Hydroxylapatite is found in a number of places as thin white coatings and small nodules. In the Grotto Cave chamber of Chifley Cave, hydroxylapatite has formed under ardealite 'potatoes', and occurs with crandallite. It is part of a complex phosphate mineral mixture in Katie's Bower, Chifley Cave. In Lucas Cave, traces are present on walls near The Slide; in layers below the 'potatoes'; lining a solution tube in limestone above the 'potatoes'; and with crandallite in Bone Cave. It has also been found on cave earth

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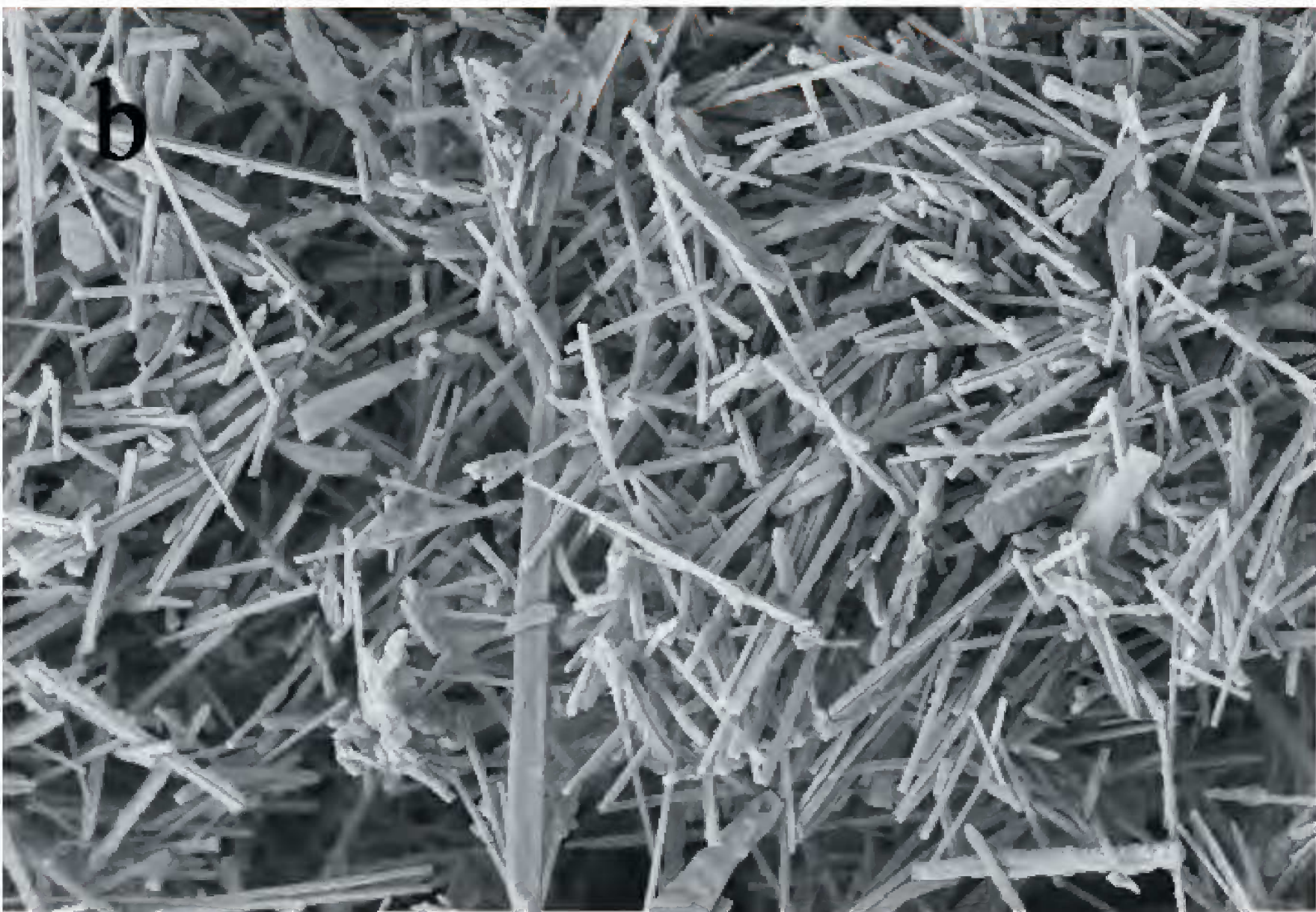


Figure 3a,b: a: Calcite fluff growth, Wilkinson Branch of Chifley Cave, width 6 cm. Image: Ross Pogson; b: SEM image, calcite fluff growth, Wilkinson Branch, Chifley Cave. Field of view 141 x 98 microns. Image: Sue Lindsay, Australian Museum



Figure 4: Aragonite, Chevalier Cave. Image: Ted Matthews, Jenolan Caves



Figure 5: Ankerite veins in limestone, 30 m south of eastern entrance to Grand Arch. View approx. 20 x 15 cm. Image: Ross Pogson, Australian Museum



Figure 6: SEM image, Mg-rich moonmilk, Lyrebird's Nest Chamber, Ribbon Cave. Field of view 50 x 35 microns. Image: Sue Lindsay, Australian Museum

coating limestone in Queen Esther's Chamber, River Cave. The CO₂-rich variety ('carbonate-hydroxylapatite') occurs in Katie's Bower, Chifley Cave, as amber botryoidal crusts of 0.5 mm spherules. Hydroxylapatite is present in altered bat guano collected by Wiburd in 1898 from Lucinda Cavern, Chifley Cave (DR12132) and in altered guano collected more recently from the Exhibition Chamber of Lucas Cave. It is also intermixed with other phosphate minerals elsewhere.

Crandallite

Crandallite forms a white, chalky, crumbly deposit in the Bone Cave section of Lucas Cave, collected by guides from floor deposits (D58074). In Chifley Cave it occurs as a white crumbly nodular deposit (D56949) (Fig. 9) on red-brown clay on limestone, above the 'potatoes' alcove in the Grotto Cave (Pogson et al. 2011), and as a component of phosphates in Katie's Bower.

Other phosphates – Katie's Bower, Chifley Cave (Taranakite, Variscite, Montgomeryite, Kingsmountite, Leucophosphite)

These five phosphate minerals, together with hydroxylapatite, CO₂-rich hydroxylapatite, crandallite, calcite, silica, and horizontally-stratified clays (kaolinite, illite) have been identified in Katie's Bower, Chifley Cave, as complex intergrowths in a prominent poorly-consolidated, unstable outcrop. This deposit has slumped downwards and forward, obscuring contacts and extending under the path and down a gentle slope to the opposite cave wall. Many of the phosphates fluoresce pale yellow under short-wave ultraviolet light.

Mingaye (1898) reported and analysed phosphates from this location, including taranakite (then called 'minervite') in 'Left and Right Imperial Caves'. As to their origin, Wiburd found mineralised bat guano in Lucinda Cavern, Chifley Cave (his donated specimen DR12132). Taranakite, hydroxylapatite, leucophosphite and variscite (D58072) form crumbly, fine-grained white to cream-coloured chalky masses and irregular veins and coatings. An iron-bearing variety of variscite is also present (KB19). A taranakite specimen (misidentified at the time as 'sulphate of alumina') (D10948) was found in 'New Cave' (probably Jubilee Cave) by Robert Etheridge,

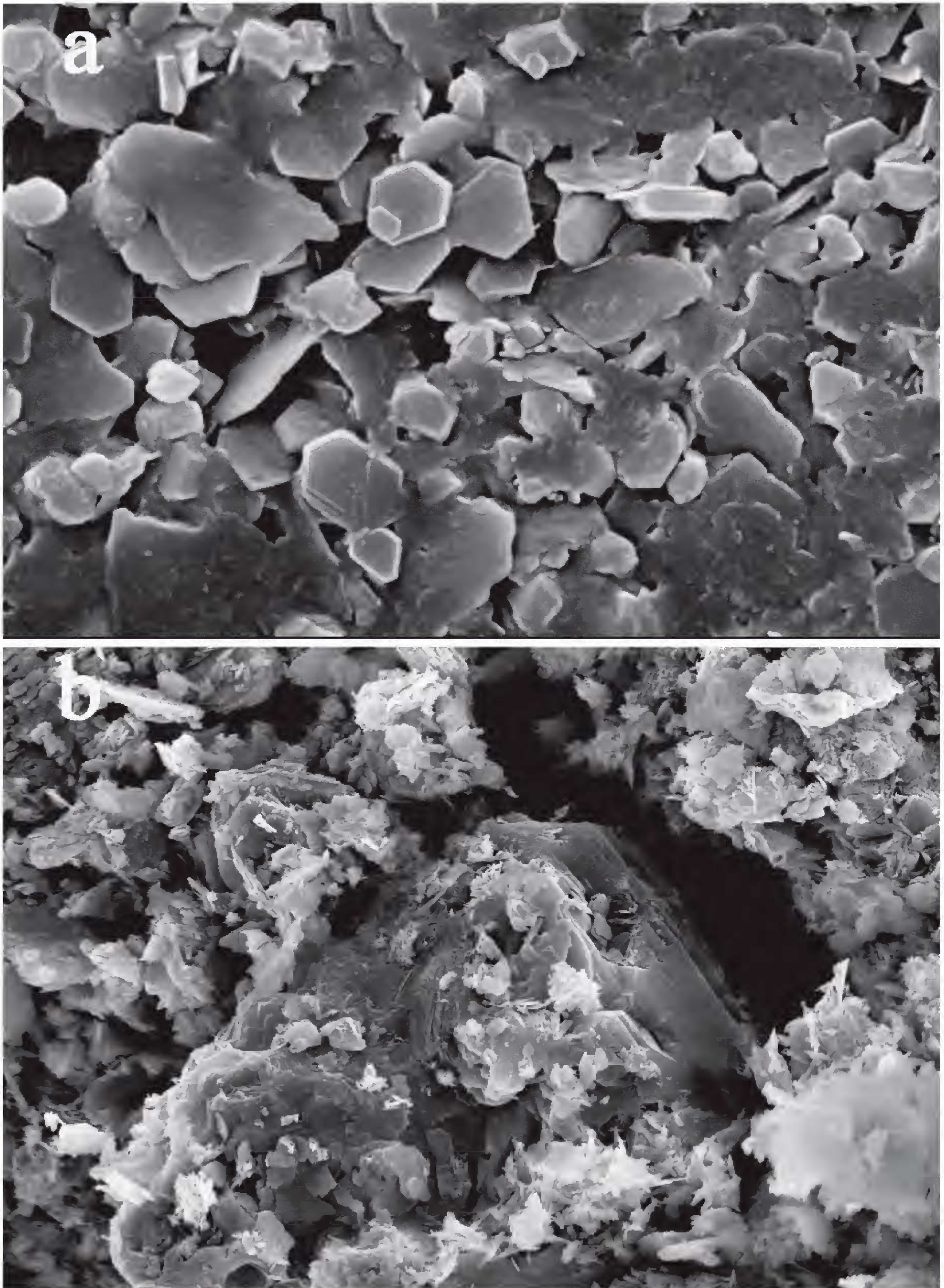


Figure 7a,b: SEM images, a: Kaolinite crystals (JRV7), River Lethe, River Cave, field of view 20 x 14 microns; b: Illite on kaolinite (JRV9), The Junction, River Cave, field of view 48 x 34 microns. Images: Sue Lindsay, Australian Museum

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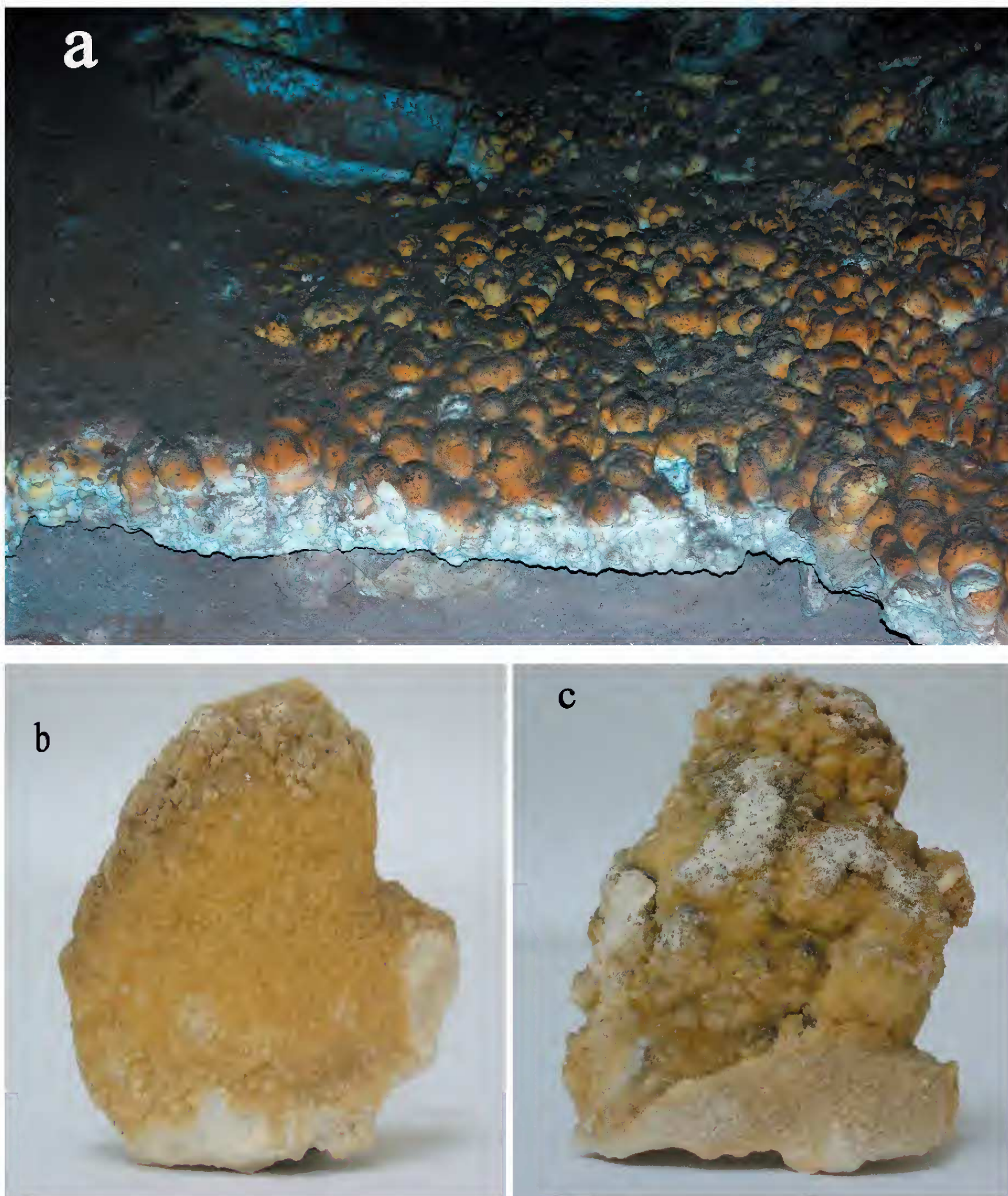


Figure 8a,b,c: a: ‘Potatoes’, Bone Cave, Lucas Cave; b: Ardealite ‘potato’, Lucas Cave (D49535), size 60 mm;. c: ‘Potatoes’, Chifley Cave (D57257), size 70 mm. Images: Ross Pogson, Australian Museum

Australian Museum in 1896. Taranakite is uncommon in Australia, but Bridge (1967) reported it from caves near Jurien Bay, and on the Nambung River, Western Australia.

Montgomeryite is the Mg-analogue of kingsmountite (Anthony et al. 2000). Montgomeryite

forms tiny rosettes of pale yellow platy crystals 0.05 – 0.3 mm and micro-botryoidal aggregates similar to those of kingsmountite, in small crystal-lined cavities in white chalky matrix, and as a minor component of massive, crumbly, chalky mixed phosphates. Additional tests by Frost et al. (2012a) confirmed the identification as montgomeryite (D58702, D58703).

Kingsmountite forms white radiating thinly bladed to acicular microcrystals with silky lustre, in compact aggregates of spherules 2 – 3 mm. It also forms larger bladed microcrystals in crusts up to a 4 mm thick (D58703). Blocky fawn-coloured crystals less than 0.5 up to 1 mm line small vughs in fine-grained crumbly, chalky matrix. It is closely associated with montgomeryite. SEM images show the kingsmountite rosettes are made of 2 – 3 micron crystal plates (Fig. 10).

Gypsum

Gypsum forms the yellow outer shell of the ‘potatoes’ in Lucas Cave (Bone Cave section) and in Chifley Cave (Grotto Cave section). Mingaye (1898, 1899) analysed the Grotto Cave deposit and identified the material as gypsum. It is also found as white to colourless deposits elsewhere in small cavities in upper Bone Cave, and crusts in Centenary Cave, in Lucas Cave. Minor deposits also occur in other caves. In the past, gypsum has been found as white to clear masses and curved, fibrous crystal groups (gypsum ‘flowers’) associated with palaeokarst (D19994) in the Devil’s Coach House. Their original collection site in the Devil’s Coach House is unknown but gypsum specimens from this locality are preserved in the Australian Museum collections (D19994, D12021) (Fig. 11a,b).

Silica (quartz, cristobalite, amorphous)

Silica is present as small quartz grains in many clays and cave sediments. It also occurs as minor poorly crystalline cristobalite and amorphous silica in mixed phosphates; in fluffy calcite growths in the Wilkinson Branch of Chifley Cave; and in Mg-rich moonmilk in Ribbon Cave.

Romanèchite

Romanèchite is present as thin black to brown-black surface coatings in many places. It is also present as tiny rounded black nodules to 1.5 mm in clays.

Goethite and hematite

Goethite and hematite are widespread. They are present in red, brown and yellow clays, and also stain calcite speleothems in a variety of colours. Extensive concretionary goethite deposits, often as ‘pipe concretions’ are seen near the far end of Jubilee Cave.

Niter and sylvite

Niter was reported by Wilkinson (1886) from the Grand Arch, and by Mingaye (1898, 1899) from

the Devil’s Coach House. More recently, Sydney University researchers (J. James pers. comm.) found niter and tiny cubic crystals of sylvite in dust from the SW side of the Grand Arch. Jenolan Caves staff found thick crusts of white material, later identified as niter, from Dust Cave high up on the south side of Grand Arch. Dust Cave is a 9 x 7 x 2 m cavity just to the right of the top of the Lucas Cave path, partly in between large limestone boulders fallen from the roof. The cave walls consist of limestone boulders and bedrock, conglomerate cave fill and lithified palaeokarst.

The niter crusts in Dust Cave are horizontal deposits on the cave floor, partly covered by a large pile of fine grey-brown dust. Small crusts and stalactites of niter occur on the cave walls, especially on porous conglomeratic cave fill. These niter crusts are up to 5 cm thick (D52263) and have a corroded appearance, best seen in cross-section (Fig. 12). The corrosion channels run perpendicular to the horizontal crust surface. The crusts contain skeletal crystals of sylvite 0.1 - 3 mm (average 0.3 mm), sometimes occurring in long strings perpendicular to the horizontal surface of the crusts. The sylvite content of the crusts is variable, ranging from 5–15 % by volume (Colchester et al. 2001). Crevice fillings of niter occur in several places in the Grand Arch.

DISCUSSION

Carbonates

The calcite speleothems are usually very pure calcium carbonate but can be stained various colours by iron oxides and hydroxides, manganese oxides and organic material. Calcite can also contain magnesium, manganese, strontium and iron in its crystal structure.

Formation of the calcite-rich fluffy growths is still a matter for debate. Suggestions have been: it formed as a part of the life cycle of bacteria, fungi or algae; it is a disintegration product of bedrock or other cave formations; or it is a precipitation directly from ground water, but special conditions promote fibrous crystal aggregates. It has also been suggested the flat calcite lamellae are pseudomorphs after metastable monohydrocalcite (hexagonal $\text{CaCO}_3 \cdot \text{H}_2\text{O}$), or that the calcite needles are paramorphs after aragonite (Onac and Ghergari 1993; Ghergari et al. 1994). These growths also occur in Chevalier, Glass, Mammoth, and Wiburd’s Lake Caves. A chemical analysis of fluffy calcite growths from Wilkinson Branch, Chifley Cave, is given in Table 2 (analysis 3).

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Figure 9: Crandallite, Grotto Cave, Chifley Cave. Size 10 x 25 cm. Image: Ross Pogson, Australian Museum

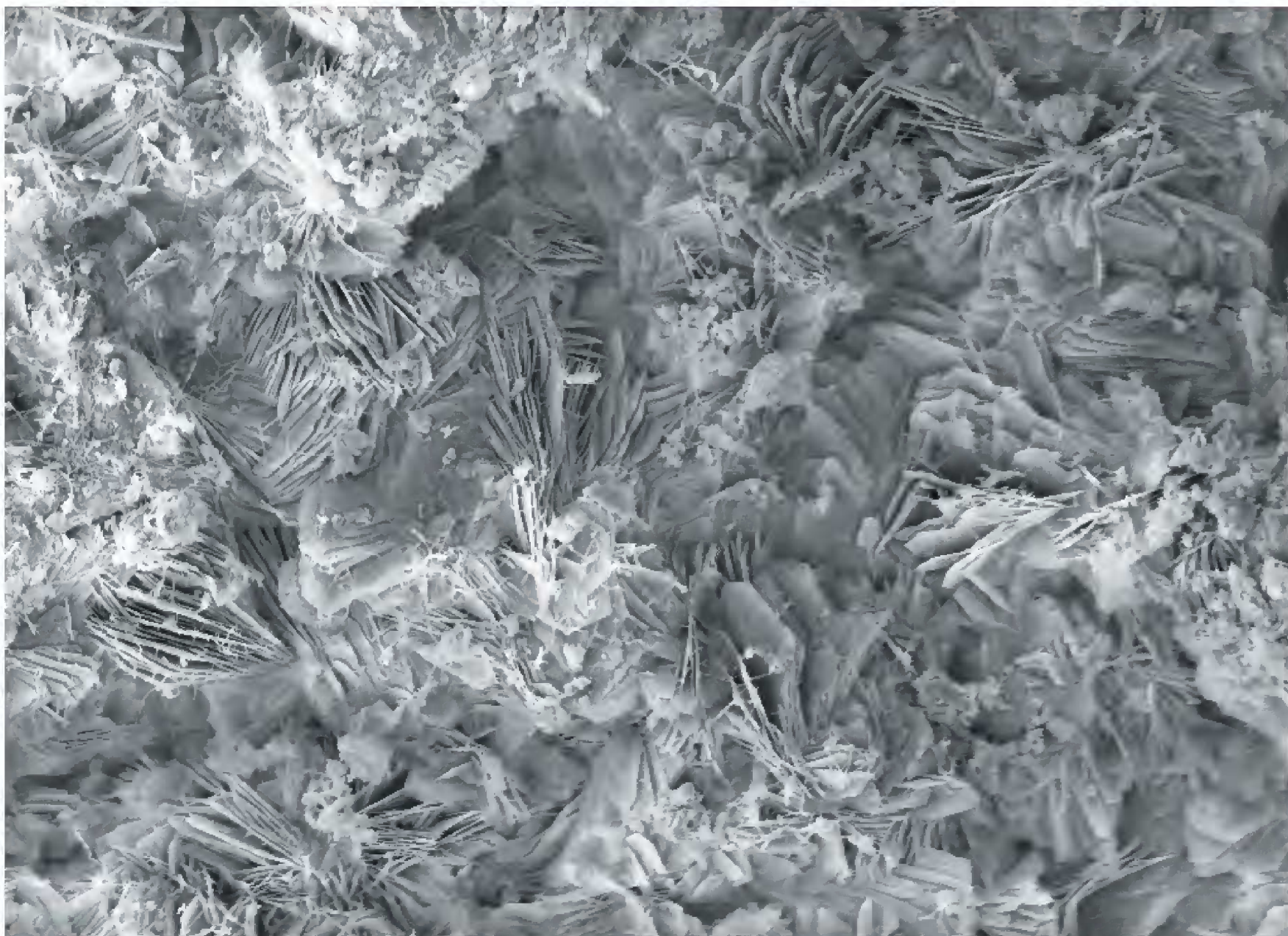


Figure 10: SEM image, Kingsmountite (D58703), Katie's Bower, Chifley Cave. Field of view 280 x 190 microns. Image: Sue Lindsay, Australian Museum

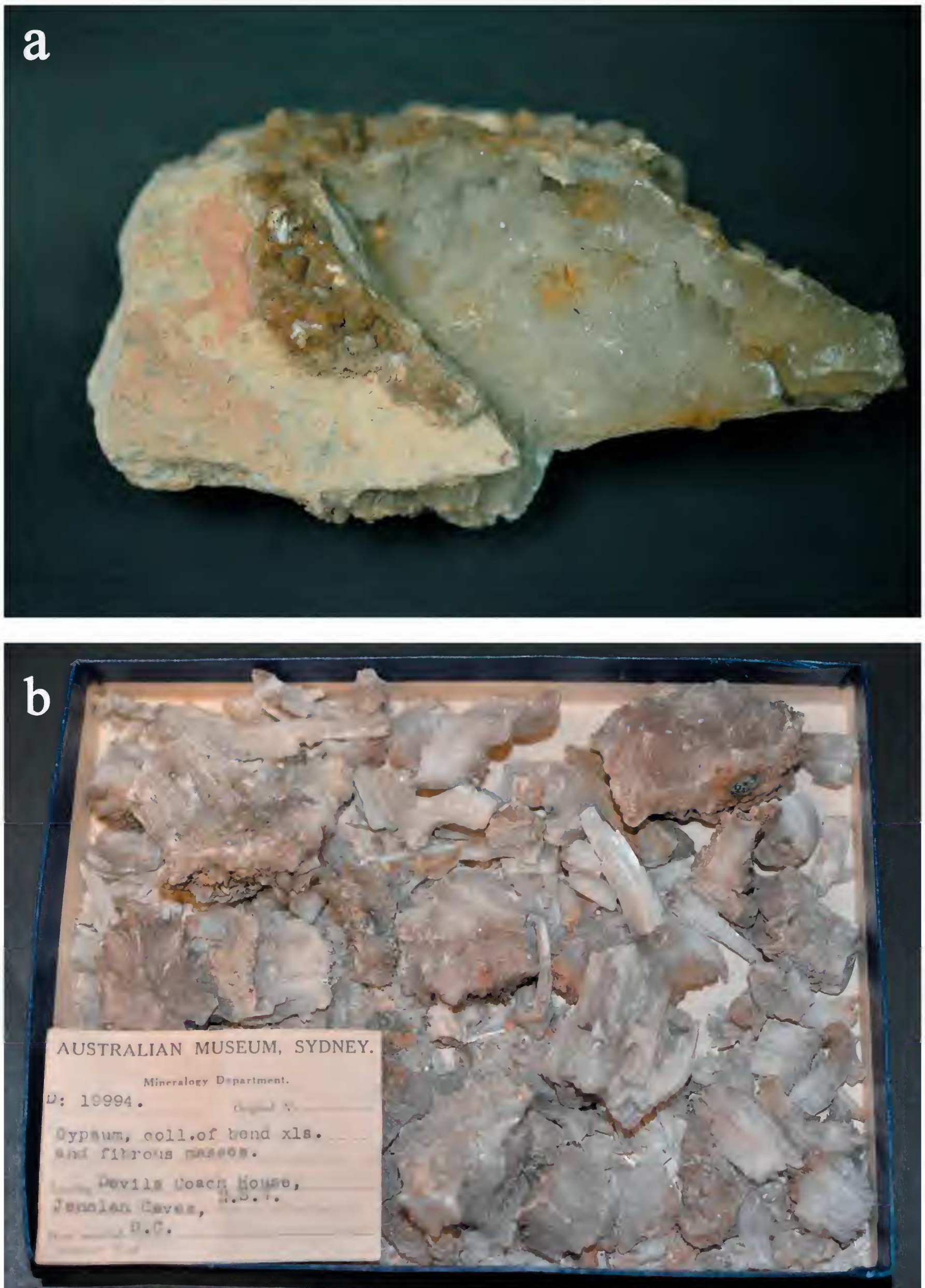


Figure 11a,b: a: Gypsum, Devils Coach House, D12021, 14 x 7 x 5 cm (with attached palaeokarst); b: Gypsum 'flowers' to 80 mm (D19994). Images: Ross Pogson, Australian Museum

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Fig. 12: Niter/sylvite crust (D52263), Dust Cave, Grand Arch. Size 7 x 5 x 5 cm. Image: Stuart Humphreys, Australian Museum

Aragonite is normally stable at higher temperatures and pressures over 3 kbar (MacDonald 1956). However, it forms in caves at ambient pressures and temperatures, (approximately 15°C and 1 bar), which is outside its thermodynamic stability field. Based on P/T data alone, only calcite should be present, and aragonite will very slowly alter to calcite but seems to persist for a long time in caves. It is widely thought that aragonite is formed when calcite precipitation is inhibited by structural poisons like Sr, Fe, Mg, phosphate and sulfate ions, but other factors, such as low drip rates, low evaporation rates, and variations in temperature, atmospheric humidity and carbon dioxide concentration may be involved. If the presence of Mg ions is a factor in its formation, possible Mg sources are nearby dolomite or ankerite. Jenolan aragonite has approximately 0.3% SrO as well as minor Mg, Fe, P etc. (Table 2, analyses 1 and 2).

The ankerite and dolomite have variable chemistry. They are more susceptible than limestone to alteration, and it is possible that much of the soggy goethite-bearing clay deposits in caves along McKeown's Valley, near the western limestone contacts were formerly iron-bearing dolomites. Much of the horizontally-bedded Carboniferous carbonate palaeokarst (caymanite) in The Mud Tunnels,

River Cave is dolomitic. Some of this palaeokarst contained pyrite (now altered to goethite), and square crystal outlines can be seen in thin-section. Compositions of Fe-rich dolomite from near the entrance of the Lyrebird's Nest Chamber, Ribbon Cave; and from Contact Cave near the western edge of the Jenolan Caves Limestone, are shown in Table 2, analyses 4 and 5.

Mg-rich 'moonmilk', a mixture of microcrystalline magnesium-bearing carbonates, is often found in close proximity to aragonite, or dolomite and ankerite. The dolomite is often decomposed to a goethite or hematite-rich clay, obscuring its carbonate origins. The decomposition of these Mg-rich minerals provides the sources of Mg²⁺ ions in solution required for formation of huntite and hydromagnesite. These minerals are precipitated when magnesium ion concentration increases with evaporation (Hill and Forti 1997).

Clays

The clay deposits appear to represent different ages and origins. Younger clays may originate from wind-blown dust (loess), or water-borne sediments brought in by streams or floodwaters. However, some of the older clays appear to have components of altered, reworked volcanic ash detritus washed or blown into the caves. This volcanic detritus is present in River Lethe clay, River Cave. Some of the clay deposits may have formed as alteration products resulting from ascending hydrothermal fluids. The evidence for presence of upwelling hydrothermal fluid activity is based on the analysis of cupola morphology by Osborne (1999). Large deposits of water-bearing goethite-rich clays occurring in caves along McKeown's Valley, near the western edge of the Jenolan Caves Limestone may represent altered dolomitised limestone bedrock.

The potassium content of K-deficient muscovite ('illite') made Potassium-Argon dating possible, and a range of illite-bearing clays gave Carboniferous dates of 320-357 Ma (mean 337 Ma) (Visean to Namurian). Details of the K-Ar dating results are presented in Osborne et al. (2006, Table 5). Fission track dating of zircon grains extracted from clay from The Junction, River Cave, gave a central age of 308.9±25.6 Ma with two age groups with pooled ages of 435.9±19.1 Ma (Carboniferous) and 207.2±18.5 Ma (Late Triassic to Early Jurassic) (Green

Table 2: Analyses of some Jenolan Caves aragonite, calcite and dolomite (XRF wt%)

1. Aragonite (JRV2) from a stalactite near the Furze Bush chamber, Mud Tunnels, River Cave.
2. Aragonite (JR7A) from crystal spheres, Lyrebird's Nest Chamber, Ribbon Cave.
3. Calcite fluffy growth (W1), from Wilkinson Branch, Chifley Cave.
4. Dolomite, iron-bearing (J167), near entrance of Lyrebird's Chamber, Ribbon Cave.
5. Dolomite, iron-bearing (JC3), from a stalactite in Contact Cave.

Analyst: Marie Anast, University of Technology, Sydney, by X-ray fluorescence (total Fe as Fe₂O₃)

	1	2	3	4	5
SiO ₂	0.14	7.1	0.79	5.8	11.7
TiO ₂		0.35	0.02	0.37	0.11
Al ₂ O ₃	0.07	3.5	0.35	3.64	5.1
MnO		0.46	0.02	0.87	0.07
Fe ₂ O ₃	0.08	3.29	0.45	6.8	2.47
MgO		0.86	0.23	9.2	5.7
K ₂ O	0.02	1.4	0.11	1.62	1.58
CaO	99.3	82.6	97.5	71.3	72.4
BaO	0.02	0.03			0.27
SrO	0.26	0.28	0.03	0.06	0.35
P ₂ O ₅		0.15	0.29	0.24	0.09
SO ₃		0.04	0.10	0.10	0.04
Total	99.9	100.0	99.9	100.0	99.9

2003). Details of the fission track dating results are presented in Osborne et al. (2006, Table 6). It is suggested in Osborne et al. (2006) that some of these Carboniferous clays and their associated sand-size fraction (pyroclastic rock fragments, pyroxenes, zircons and illite pseudomorphs after feldspar) have a common origin, likely derived from reworked local Carboniferous volcanoclastics. The pristine crystal forms of both kaolinite and illite in several Jenolan clay deposits indicate that they have been allowed to grow in situ, undisturbed (Figs 7a,b).

Phosphates

Pogson et al. (2011) suggested that the ardealite 'potatoes' in Lucas and Chifley Caves have grown vertically from a sloping surface, under subaerial conditions, growing upwards from their porous substrate base by evaporation of vertically-drawn pore water (wicking). Their morphology and mode of occurrence make formation in a pool or by dripping water less likely. Sulfur isotopes in ardealite gave $\delta^{34}\text{S}$ of +11.12 to +12.8 ‰ (Pogson et al. 2011, Table 3), suggesting that sulfate-rich solutions came from leaching of bat guano deposits (at Jenolan from the bent-wing bat, *Miniopterus schreibersii*). These

mineralised solutions reacted with limestone (Pogson et al. 2011). Most cave phosphate minerals originate from guano, which can also be a source of sulfur (Hill and Forti 2004). There is currently no visible bat guano near the 'potatoes' in Lucas Cave, although old deposits do occur in the Exhibition Chamber in another part of the Lucas Cave system. Ardealite chemical analyses are presented in Pogson et al. (2011, Table 2). Identification was confirmed by additional analytical methods (Frost et al. 2011a, 2012b).

Hydroxylapatite was probably a precursor mineral in the formation of other phosphates from leached bat guano (Marincea et al. 2004), being altered by changes in ion concentrations, Eh, pH and temperature of the percolating solutions. Crandallite is often an earlier-formed phosphate. Additional confirmatory tests for this Jenolan crandallite are detailed in Frost et al. (2011b, 2012c).

The complex aluminium, calcium and potassium-bearing phosphate minerals of Katie's Bower, Chifley Cave formed from reaction of acidic phosphatic solutions leached from bat guano, with limestone and cave clays. The phosphate deposits are complex mixtures of fine-grained minerals, making XRD identification difficult. Although bat guano was

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found in the 19th Century in the Lucinda Cavern of Chifley Cave, no recognisable guano traces remain in Katie's Bower. This suggests the mineral assemblage represents the final stage of guano alteration, consistent with pH levels approaching neutral (Vince et al. 1993). The chemical reactions have also released amorphous silica.

Variscite can be formed by leaching of montgomeryite with the loss of calcium (Hill and Forti 1997). Kingsmountite (Dunn et al. 1979) is a rare mineral. It is even rarer in cave environments, being previously reported only from Rossillo Cave, Mexico (Forti et al. 2006), although it occurs in USA, Russia, Portugal, Germany, and South Australia in other types of phosphate deposits (Anthony et al. 2000).

Onac and Veres (2003) and Marincea et al (2004) discussed formation of phosphates in Romanian caves, finding that ardealite could form from pre-existing hydroxylapatite. In general, the phosphates were formed from phosphate-rich, then sulfate-rich solutions, accompanied by pH changes reflecting the degree of carbonate dissolution. Hydroxylapatite usually forms at higher pH, and is destabilised for pH values up to 5.5, but if sulfur is available under those conditions, ardealite formation is favoured. Taranakite forms early under damp conditions in the presence of excess potassium, from solutions with pH < 6. Vince et al. (1993) studied the paragenesis of phosphate minerals at the Parwan Cave in Victoria, Australia, finding that taranakite and clay formed early, with apatite later, and finally montgomeryite. An additional confirmatory test for Jenolan taranakite is detailed in Frost et al. (2011c).

Sulfates

Gypsum was considered the second most common cave mineral by White (1976) and Onac (2005), and the third most common after calcite and aragonite by Hill and Forti (1997). Gypsum sulfur isotope signatures from Lucas and Chifley Cave 'potatoes' gave a $\delta^{34}\text{S}$ of +11.3 to +11.8 ‰, indicating an organic origin, derived from bat guano (possibly via sulfur-oxidising bacteria in the guano). Sulfur isotopes from gypsum in the Devil's Coach House deposits ($\delta^{34}\text{S}$ of +1.4 to +4.9 ‰) indicate an inorganic origin, probably from breakdown of pyrite in carbonate palaeokarst. This interpretation of the isotope data is discussed in Pogson et al. (2011, Table 2).

Oxides and hydroxides

Apart from quartz sand grains, silica is widespread as a minor microcrystalline or cryptocrystalline component of many cave minerals, and it has also

been released by chemical alteration of clays by acidic phosphatic solutions, giving rise to poorly crystalline cristobalite, as well as amorphous silica. Hematite and goethite in the caves may have originated from a variety of processes, including the breakdown of iron-bearing carbonates and pyrite, ferruginous wind-blown dust, and deposition from percolating iron-rich solutions. The high barium content of the clays (0.05 – 0.096 wt%) is due to the presence of romanèchite, which occurs as small rounded concretionary nodules, and is also common as thin films and coatings elsewhere (Osborne et al. 2006).

Nitrates and chlorides

The dust pile in Dust Cave is leached, powdery dung from the brush-tailed rock wallaby *Petrogale penicillata*. Waters percolating through the dung have leached nitrates and chlorides and redeposited them as niter and sylvite. The Grand Arch is very dry, and in winter cold, dry westerly winds blow straight through, promoting evaporation and deposition of the niter and sylvite crusts. The sylvite was deposited after the niter, filling some of the vertical cavities between the niter crystals (Colchester et al. 2001).

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